

MEMBRANE FABRICATION AND MODIFICATION FOR THE TREATMENT OF WASTEWATER USING MEMBRANE DISTILLATION

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CERTIFICATE OF ORIGINAL AUTHORSHIP

I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree except as part of the collaborative doctoral degree and/or fully acknowledged within the text. I also certify that the thesis has been written by me.

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ABSTRACT

Owing to both water shortage and environmental protection, the government around the world is creating policies to regulate the release of wastewater into natural bodies of water. Therefore, there is a growing requirement of highly efficient wastewater treatment technologies.

Currently, centralized wastewater treatment plants were used in most cities and towns globally. The on-site treatment of domestic wastewater is consistently gaining interests because it reduces the needs of central treatment plants, which require large footprint and high maintenance. In addition, the potential use of the reclaimed water for non-potable purposes reduces the stress in local water supply, and hence the cost of freshwater production and transportation. However, conventional wastewater treatment technologies used in the centralized treatment plant are not feasible to be implemented in the decentralized treatment facilities owing to its large footprint and long retention time. Currently membrane bioreactor (MBR) has been developed for wastewater treatment facilities with small footprint. However, the quality of permeate discharged from MBR system is not high enough for direct use. Therefore, additional treatment such as UV and reverse osmosis (RO) are essential, which requiring more footprint and energy consumption. To address these issues, the overall aim of my PhD study is to develop highly efficient membrane system to treat wastewater with special designed membranes. Membrane distillation (MD) has many advantages over conventional microfiltration (MF) such as high quality permeates, leading to potentially high energy efficiency for the whole wastewater treatment plant. So, it is critical to evaluate the possibility of MD to replace MF in MBR, as MD has unique mechanism which provides several advantages over MF. Hereby, following research objectives have been developed to meet the aim: 1. to develop the first thermophilic anaerobic membrane distillation bioreactor (anMDBR) for the treatment of municipal wastewater. 2. to improve the permeation performance of hollow fiber membranes. 3. to investigate the behavior (mass transport, fouling, and rejection) of organic compounds in MD processes regarding fouling and mass transfer.

During my PhD studies, I have successfully developed the first anMDBR system in lab-scale. High inorganic and organic compounds rejection of 99.99% could be achieved using this system. Based on the results, I recommend 45 °C as optimal bioreactor temperatures for its stable flux performance and resource recovery. It was found that salinity of the mixed liquor had minimal impact on anMDBR. The potential recovery of biogas and volatile fatty acids

offered economic benefits. Some challenges were realized when developing an MDBR system:

1. Permeation flux was very low (~2 LMH).
2. Impact of volatile organic compounds (VOCs).
3. Membrane fouling issues.

Hence, following solutions have been suggested:

1. Development of membrane with high permeability.
2. Study of VOCs behavior.
3. Development of membranes with anti-fouling properties.

Therefore, in next stage of my study, I developed hollow fiber membranes with bicontinuous structure and porous skin without using weak solvent in coagulation bath. The open pore morphology improved permeation performance in membrane distillation due to high porosity and mean pore size. Also, I found that non-solvents in the dope solution affect the morphology of hollow fiber membranes. It can be concluded that this is a simple and cost-effective technique, which is suitable for mass production. Then I investigated the behavior of VOCs in feed tank. It was found that VOCs with surfactant properties existing in the feed have high mobility and could cause rapid wetting. Also, the total flux of VMD was increased with the addition of VOCs into the feed. And VOCs showed negative impacts on the permeate quality as they could penetrate membranes. I also conducted some research regarding permeation performance improvement using heat-treatment and optimal conditions had been determined. Recommendations for future study have also been addressed in this thesis.

LIST OF ABBREVIATIONS

2-BE	2-Butoxyethanol
anMDBR	anaerobic membrane distillation bioreactor
AF	Anti-fouling
AgNP _s	Silver nanoparticles
AFM	Atomic force microscopy
AGMD	Air gap membrane distillation
Al ₂ O ₃ NPs	Alumina nanoparticles
ATR-FTIR	Attenuated total reflectance – Fourier transform infrared spectroscopy
AW	Anti-wetting
BAU	Business as usual
C ₆ Cl ₃	Alcyone
CA	Contact angle
CBD	Chemical bath deposition
CDI	Capacitive deionization
CF ₄	Tetrafluoromethane
CFP	Capillary flow porometry
CNTs	Carbon nanotubes
COD	Chemical oxygen demand
CSG	Coal seam gas
CVD	Chemical vapor decomposition
DBP	Dibutyl phthalate
DCMD	Direct contact membrane distillation
DI	De-ionized water
DMAc	N, N-Dimethylacetamide
DMF	N, N-Dimethylformamide
DS	Desalination
DSC	Differential scanning calorimetry
EDX	Energy dispersive x-ray spectroscopy
ENM	Electrospun nanofiber membrane
FAS17	1H, 1H, 2H, 2H-Perfluorodecyltrimethoxysilane
FAS21	1H, 1H, 2H, 2H-Perfluorododecyltrichlorosilane

FO	Forward osmosis
FDTS	1H, 1H, 2H, 2H-Perfluorodecyltrichlorosilane
FTCS	1H, 1H, 2H, 2H-Perfluorododecyltrichlorosilane
GC-MS	Gas chromatography-mass spectrometry
GOR	Gain output ratio
HA	Humic acid
HF	Hollow fiber
HP	High permeability
IPA	Isopropyl alcohol
IW	Industrial wastewater
LBL	Layer-by-layer
LEP	Liquid entry pressure
LNG	Liquefied natural gas
L-L	Liquid-liquid
MBR	Membrane bioreactor
MCr	Membrane crystallization
MD-BR	Membrane distillation-membrane bioreactor
MD	Membrane distillation
MF	Microfiltration
N6	Nylon-6
NaCl	Sodium chloride
NaOH	Sodium hydroxide
NH ₄ ⁺	Ammonium
NIPS	Non-solvent induced phase separation
NF	Nanofiltration
NMP	N-Methyl-2-pyrrolidone
NP	Nanoparticle
NS	Non-solvent
OH	Hydroxyl
OMBR	osmosis membrane bioreactor
OTMS	Octadecyltrimethoxysilane
PA	Polyamide
PAM	Polypropylene acid ammonium

PAN	Polyacrylonitrile
PDEs	Partial differential equations
PDMS	Polydimethylsiloxane
PFDT	1H, 1H, 2H, 2H-Perfluorodecanethiol
PFOTCS	1H, 1H, 2H, 2H-Perfluorooctyl-trichlorosilane
PFOTES	1H, 1H, 2H, 2H-Perfluorooctyltriethoxysilane
PFTES	1H, 1H, 2H, 2H-Perfluorodecyltriethoxysilane
PEI	Polyetherimide
PES	Polyether sulfone
PET	Polyethylene terephthalate
PFPE	Perfluoropolyether
PGMD	Permeate gap membrane distillation
PP	Polypropylene
PRO	Pressure retarded osmosis
PS	Polystyrene
PSD	Pore size distribution
PSf	Polysulfone
PTFE	Polytetrafluoroethylene
PTFE	
-AF 2400	Poly[4,5-difluoro-2,2-bis(trifluoromethyl)-1,3-dioxole-co-tetrafluoroethylene]
PVA	Polyvinyl alcohol
PVAc	Polyvinyl acetate
PVC	Polyvinyl chloride
PVDF	Polyvinylidene fluoride
PVDF-HFP	Polyvinylidene fluoride-co-hexafluoropropylene (PVDF-co-HFP)
RO	Reverse osmosis
SDS	Sodium dodecyl sulfate
SEC	Specific energy consumption
SEM	Scanning electron microscopy
SFE	Surface free energy
SGMD	Sweeping gas membrane distillation
SiNPs	Silica nanoparticles
SiO ₂	Silicon dioxide

SMM	Surface modifying macromolecules
SWRO	Seawater reverse osmosis
S-L	Solid-liquid
TEM	Transmission electron microscopy
TEP	Triethyl phosphate
TIPS	Thermally induced phase separation
TiO ₂	Titanium oxide
TGA	Thermogravimetric analysis
TOC	Total organic carbon
TPC	Temperature polarization coefficient
TiO ₂	Titanium dioxide
UF	Ultrafiltration
VFA	Volatile fatty acids
VIPS	Vapor induced phase separation
VMD	Vacuum membrane distillation
VOC	Volatile organic compound
x-DVLO	Extended Derjaguin Landau Verwey Overbeek
XRD	X-ray diffraction
ZnO NPs	Zinc oxide nanoparticles

LIST OF SYMBOLS

A	Effective area of the membrane
B	Pore geometry coefficient
B'	Membrane coefficient
C	Cold fluid
C_p	Permeate concentration
C_f	Feed concentration
C_m	Membrane mass transfer coefficient
C_p	Specific heat capacity
D_{AB}	Water vapor diffusion coefficient
d_h	Equivalent hydraulic diameter
f	fraction of solid surface projections under liquid droplets
$Flux_E$	Flux of each point
$Flux_I$	Flux of the initial point
g	Gravity
h	Heat transfer coefficient
H	Hot fluid
I_D	D band
I_G	G band
J	Water vapor flux
J_{AGMD}	Water vapor flux by AGMD
J/J_o	Normalized flux
k_x	Transversal thermal conductivity
k_z	Axial thermal conductivity
L	Channel length
LMH	L/m ² h
M_w	Molecular mass of water
P_{avgm}	Log mean air pressure based from both sides of the membrane
P_{avgma}	Log mean air pressure within the air gap
P_C	Water vapor pressure on the air gap layer
P_H	Water vapor pressure on the membrane surface
P_0	Water vapor pressure in the vacuum side

$P_v(T'_w)$	Water vapor pressure at the membrane shell surface at the relative temperature
Pr	Prandtl number
P_T	Total pressure of water vapor and air
P_w	Vapor pressure of pure water
r	Membrane pore radius
r_f	Roughness ratio of wetted areas
R	Universal gas constant
R_a	Mean roughness
R_{AGMD}	Total mass transfer resistance in the AGMD
γ_L	Surface tension of liquid in contact with air
γ_{SL}	Solid-liquid interfacial energy
γ_{SV}	Solid-vapor interfacial energy
γ_{LV}	Liquid-vapor interfacial energy
Re	Reynolds number
R_c	Cake layer resistance
R_G	Molecular diffusion resistance related with the graphene effect
R_K	Knudsen diffusion resistance
R_m	Membrane resistance
R_M	Molecular diffusion resistance
R_{M-air}	Molecular diffusion resistance in the air gap
R_t	Total mass transfer resistance
R_{tp}	Temperature polarization resistance
RT	Room temperature
SR	Salt rejection ratio
$T_{avg,a}$	Average temperature based from both sides of the membrane
$T_{avg,m}$	Average temperature at the air gap
u	Flow velocity
W_1	Weight of the saturated membrane
W_2	Weight of the dry membrane
x_{NaCl}	Mole fraction of NaCl
x_w	Mole fraction of water
β	Enrichment factor
t	Operating duration

γ_w	Activity coefficient of water
δ	Thickness
τ	Pore tortuosity
δ_m	Membrane thickness
δ_a	Air gap thickness
θ_Y	Young contact angle
θ_C	Apparent contact angle
Δg	Mass of permeate
ε	Membrane porosity
k	Thermal conductivity
λ	Latent heat of water
μ	Viscosity
ρ	Liquid density
ρ_e	Density of ethanol
ρ_d	Density of PVDF material
τ_m	Membrane pore tortuosity
f	Feed
fl	Fluid
m	Porous membrane
si	Solid membrane
Φ_{outer}	Outer diameter
Φ_{inner}	Inner diameter

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